A NEW EMPIRICAL APPROACH TO QUANTIFYING THE RELEASE OF ARSENIC AND SELENIUM FROM COAL FLY ASH INTO NATURAL FRESH WATERS

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INTRODUCTION

Coal fly ash (CFA) enters the environment via losses during handling, transportation and processing, and via unintended direct releases, such as the huge Kingston Fossil Plant spill in December 2008. Upon contact with natural waters, CFA may release a range of bioactive trace elements. In this context, environmental studies have largely focused on the leaching of trace elements from CFA in landfills by rainwater and groundwater, with relatively little attention to the release of these species from CFA that enters rivers and lakes. Moreover, results of the batch leaching methods typically used to study the interaction of CFA with rainwater and groundwater in landfills are not readily extrapolated to rivers and lakes, where the effective solution-to-particle mass ratio is typically high.

To address this issue, we have adapted a flow-through leaching method that was developed to examine the dissolution of trace elements from mineral aerosols deposited in the ocean. We argue that this rapid leaching technique more closely resembles the interaction of CFA with natural fresh waters, thus allowing us to assess the release of bioactive trace elements from CFA into rivers and lakes. Here we present results of such experiments applied to examine the interaction of two types of CFA with a range of natural fresh waters collected from the southeastern United States, focusing on the release of the potentially toxic elements arsenic (As) and selenium (Se) into solution.

MATERIALS AND METHODS

Flow-through leaching experiments were performed using fresh CFA collected by the Tennessee Valley Authority from the Kingston and Johnsonville Fossil Plants, and 0.2 µm-filtered fresh waters collected from the Emory River, TN; St. Mary's River, VA; Cypress Falls, VA; and Lake Drummond, VA, which were selected to provide leaching solutions with a broad range of pH, alkalinity, ionic strength and dissolved organic carbon concentration. Deionized water was used as a 'control' leaching solution. The experimental procedure entailed rapidly passing three successive 250 mL volumes of leaching solution over ~0.1 g of dried, homogenized CFA above a 0.4 µm polycarbonate membrane filter supported in a PFA filter tower (Fig. 1). From the three resulting 250 mL leachate solutions, subsamples were preserved for determination of trace elements, including As and Se, by high-resolution ICP-MS, verified by analysis of river water standard reference material SLRS-5.

In addition, the bulk elemental composition of the CFA was determined after microwave-assisted acid digestion, by ICP-MS analysis of the acid digest solution, verified by analysis of digested NIST standard reference material 1633c (coal fly ash). The concentrations of As and Se measured in the three leachate solutions and in the bulk CFA then allow us to calculate an operationally-defined **percent fractional solubility** of these elements in CFA with respect to each leaching solution, as follows:

$\%X_s$ = (mass X added to leachate)/(mass X in CFA) x 100

Where X is the element of interest (in this case, As or Se), and $\%X_s$ is the percent fractional solubility of X in the CFA. The thus defined fractional solubility values provide a useful metric for assessing the release of trace elements into natural waters, provided that the leaching procedure effectively mobilizes all of the water-soluble elements of interest from the CFA.

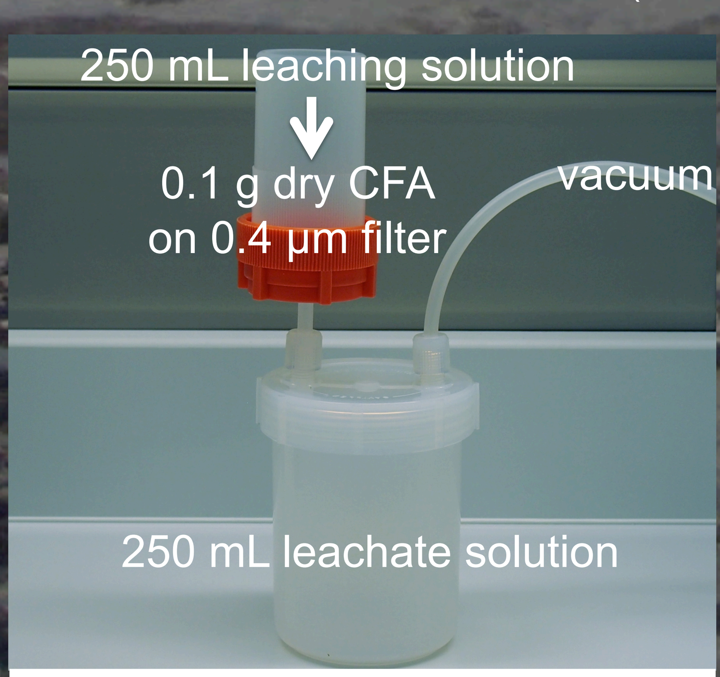

Figure 1. Apparatus used for the flow-through leaching procedure.

RESULTS AND DISCUSSION

Analyses of the trace element concentrations in each of the three successive 250 mL leachate fractions indicate that the our flow-through leaching experiments achieved varying degrees of success in terms of mobilizing (dissolving) all of the water-soluble elements of interest from the CFA. For both As and Se, the effectiveness of the leaching procedure applied to both the Kingston fly ash (Fig. 2a, 2b) and Johnsonville fly ash (Fig. 2c, 2d) was clearly dependent on the composition of the freshwater leaching solution. In the case of As, deionized water and Emory River water were apparently less effective at mobilizing As from the ash than the waters collected from Lake Drummond, the St. Mary's River and Cypress Falls (Fig. 2a, 2c). For Se, the results of the leaching experiments were less reproducible, in that there were relatively large differences between the Se concentrations measured in replicate (n = 3) leachate solutions. However, for several of the experiments, the final 250 mL of leach solution apparently mobilized the greatest amount of Se from the CFA, suggesting that larger volumes of leaching solution (or, alternately, smaller charges of CFA) are required to provide robust estimates for the fractional solubility of Se (Fig. 2b, 2d).

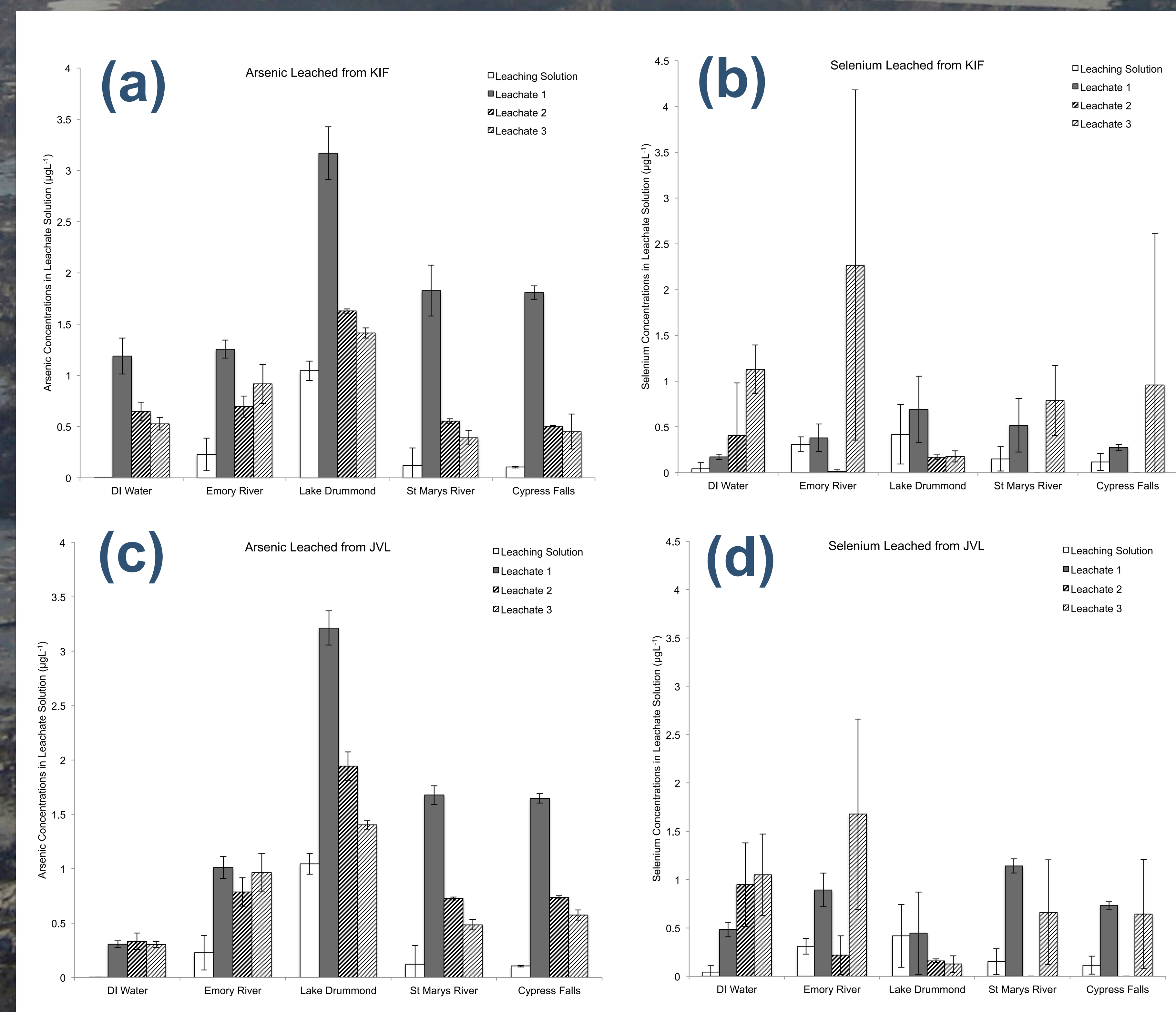

Figure 2. Mean (±1 RSD) leachate solution concentrations (µg L^{-1}) of **(a)** As leached from Kingston CFA, **(b)** Se leached from Kinston CFA, **(c)** As leached from Johnsonville CFA, and **(d)** Se leached from Johnsonville CFA. Leachate 1, Leachate 2 and Leachate 3 refer to the first, second and third 250 mL leaches, respectively, and Leaching Solution refers to the ambient concentration in the fresh water that was used as the leaching solution.

Given that the flow-through leaching procedure apparently did not mobilize all of the water-soluble As and Se from the CFA, our resulting estimates of the fractional solubility of As and Se (Fig. 3) are necessarily conservative minimum values. Nevertheless, these empirical estimates are useful as a first order estimate of the potential contamination of rivers and lakes by coal ash spills, such as the Kingston incident, and allow a comparison of the relative mobility of As and Se as a function of coal ash type, and of the composition of the receiving waters. Importantly, our data indicate that a large fraction (~50-100%) of the Se present in CFA is readily soluble in natural fresh waters, as is a significant proportion (~20%) of the As present in CFA.

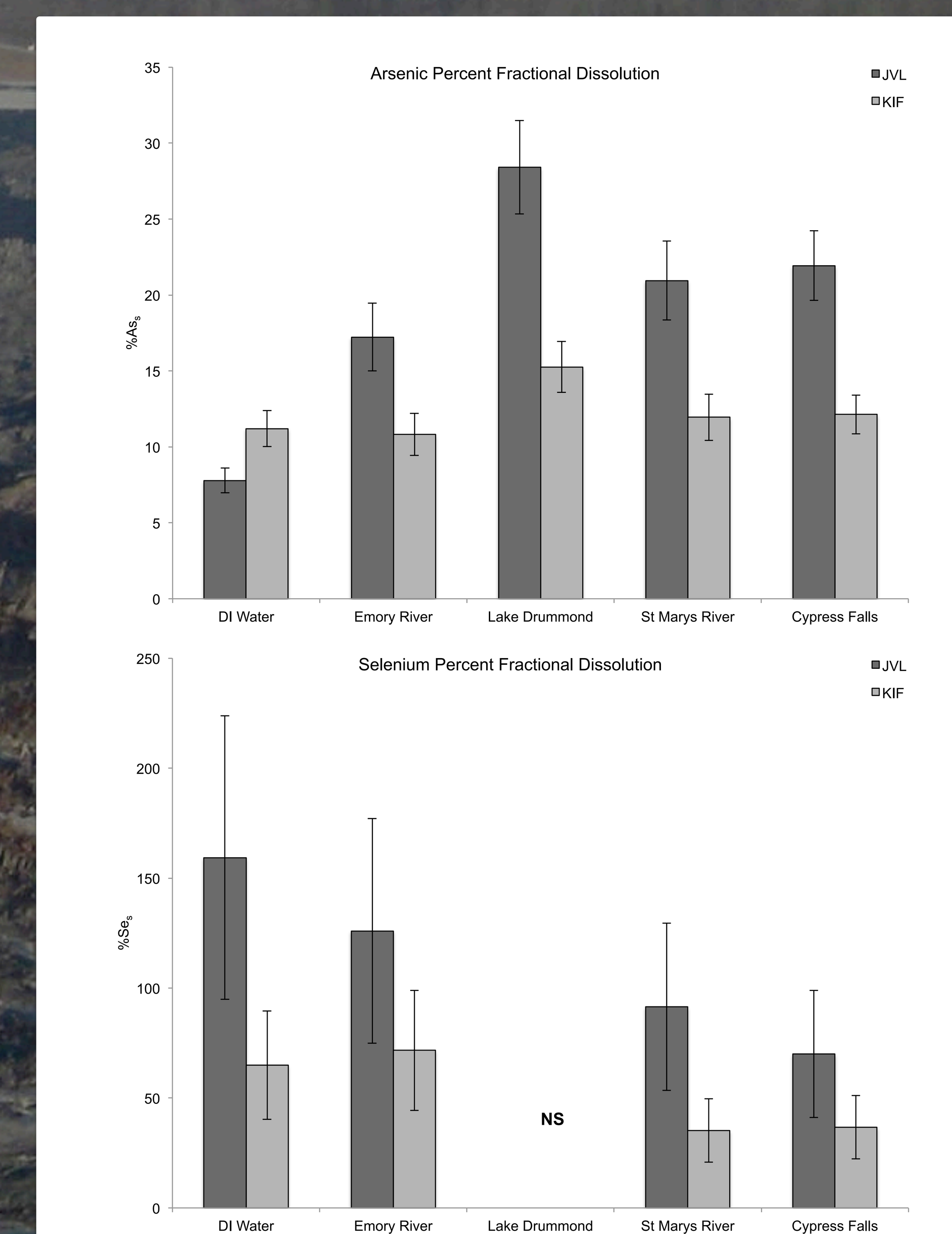

Figure 3. Calculated mean (±1 RSD) fractional solubility of As (top) and Se (bottom) in coal fly ash from Kingston (KIF) and Johnsonville (JVL).

Proposed future work will pursue modification of the leaching protocol to realize quantitative mobilization of all 'soluble' trace elements of interest from the CFA. We very gratefully acknowledge funding support from the Tennessee Valley Authority through Oak Ridge Associated Universities (award 7-22979 to PNS and GRC). We thank Neil Carriker and Bill Rogers (Tennessee Valley Authority), and Rock Vitale (Environmental Standards) for their help and advice.